

Oxidation of Zirconium Alloys in High Pressure Steam and Some Results under Atmospheric Pressure

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In order to decrease fuel-cycle costs and to improve reactor operation and spent fuel management, nuclear operators want to increase fuel discharge burnup. Due to Zircaloy-4 limitations at high burnup, PWR fuel vendors have developed and proposed the use of new zirconium alloys, such as M5TM, ZIRLOTM.

Despite the fact that worldwide used U.S. Regulatory Guide (RG) 1.157[1] §3.2.5.1 recognizes the effect of steam pressure, performance of these alloys under intermediate breaks loss-of-coolant-accident (LOCA) and higher-pressure accidental transients is poorly understood. The main first part of this paper will evaluate the database for fresh Zircaloy-4 and another alloy, reported in literature mainly after the RG 1.157 was issued[2-5]. According to plant calculations, the worst intermediate break seems to be the 3-inches break, it is characterized by a temperature above 800°C during several hundred of seconds, at a pressure between 30 and 40 bars.

Four different consistent data for fresh Zircaloy-4 show a pressure enhancement effect below 1100°C. Tests with steam/argon mixtures show that it is an effect of partial steam pressure rather than of total pressure. The consistency between results under flowing steam and stagnant steam seems to show no steam flow effect, probably the high pressure ensures good natural circulation. For fresh Zircaloy-4, the maximal relative effect occurs at 750-800°C, it coincides with temperatures at which occurs the atmospheric breakaway oxidation at longer times[6]. As for this atmospheric breakaway, the enhancement seems to be related to the tetragonal to monoclinic zirconia transformation. According to the literature, this transformation is influenced by several factors (compressive stresses, crystallite size growth, substoichiometry). For fresh Zircaloy-4 under intermediate breaks, the enhancement is not high enough to cause an actual safety problem.

Limited published data for fresh E-110TM alloy (Zr 1%Nb O-poor S-free) show, comparatively to Zircaloy-4, an increase of the temperature at which the maximal relative effect occurs[4], as for the atmospheric breakaway oxidation at longer times[7]. The enhancement is especially strong at 850°C, rapidly exceeding the embrittlement criterion under only 40 bars.

Tests with M5TM alloy (Zr 1%Nb O-rich S-doped) are under preparation and will start in 2003 in France.

No test exists for high-burnup Zircaloy-4. As there is in the literature a possible role of hydrogen on the tetragonal to monoclinic zirconia transformation, tests are necessary.

The smaller second part of this paper will be a follow-up of the 28th WRSN paper[8]. Some meetings and letters show that some fuel vendors have still difficulties to understand the tie between the worldwide used 17% ECR criterion and the Baker-Just correlation. In figure 8 of the 28th WRSN paper, it was shown how the 17% ECR value was calculated with the Baker-Just correlation. In this paper, a simulation will be made to calculate after Hobson's data what would have been the ECR value, if the U.S. Regulatory Staff had used in 1973 the Cathcart-Pawel correlation.

Finally, as Cathcart and Pawel's data are used in the CATACOMB module of the French best-estimate CATHARE code, issued from the CUPIDON code [9], and mentioned in both RG 1.157 and U.S. Research Information Letter 0202[10], some characteristics of Cathcart and Pawel's data will be pointed out in this paper.

REFERENCES

- 1) U.S. NRC, Office of Nuclear Regulatory Research, Best-estimate calculations of emergency core cooling system performance, Regulatory Guide 1.157, May 1989
- 2) Pawel, R.E.; Cathcart, J.V.; Campbell, J.J., The oxidation of Zircaloy-4 at 900 and 1100EC in high pressure steam, *Journal of Nuclear Materials* (Jun 1979). v. 82(1) p. 129-139.
- 3) Bramwell, I.L.; Worswick, D.; Parsons, P.D.; Haste, T.J., An experimental investigation into the oxidation of Zircaloy-4 at elevated pressures in the 750 to 1000EC temperature range, 10. international symposium on zirconium in the nuclear industry. Baltimore, MD (United States). 21-24 Jun 1993, ASTM STP 1245 p. 450-465.
- 4) Vrtlikova, V.; Molin, L.; Valach, M., Oxidizing and hydriding properties of Zr-1Nb cladding material in comparison with zircaloys, Technical committee meeting on influence of water chemistry on fuel cladding behaviour. Rez (Czech Republic). 4-8 Oct 1993, IAEA-TECDOC--927 p. 227-251.
- 5) Park, K.; Kim, K.; Whang, J., Pressure effects on high temperature Zircaloy-4 oxidation in steam, International topical meeting on LWR fuel performance, Park-City, Utah (United States), 10-13 April 2000, CD-ROM, poster presentations, p. 394-401
- 6) Leistikow, S.; Schanz, G., Oxidation kinetics and related phenomena of Zircaloy-4 fuel cladding exposed to high temperature steam and hydrogen-steam mixtures under PWR accident conditions, *Nuclear-Engineering-and-Design-Netherlands*. (Aug 1987). v. 103(1) p. 65-84.
- 7) Bibilashvili, Yu.K.; Sokolov, N.B.; Andreyeva-Andrievskaya, L.N.; Salatov, A.V.; Morozov, A.M., High-temperature interaction of fuel rod cladding material (Zr1%Nb alloy) with oxygen-containing mediums, Technical committee meeting on behaviour of LWR core materials under accident conditions. Dimitrovgrad (Russian Federation). 9-13 Oct 1995, IAEA-TECDOC 921 p. 117-128.
- 8) Hache, G.; Chung, H.M., The history of LOCA embrittlement criteria, 28. Water Reactor Safety Information Meeting Bethesda, MD (United States) 23-25 Oct 20001, NUREG/CP-0172 p. 205-237
- 9) Houdaille, B.; Fillatre, A.; Morize, P., Development and qualification of the LOCA analysis system CUPIDON-DEMETER, OECD-NEA-CSNI/IAEA specialists' meeting on water reactor fuel safety and fission product release in off-normal and accident conditions. Roskilde (Denmark). 16-20 May 1983, IWGFPT-16, p. 148-162.
- 10) Thadani, A.C., Revision of 10 CFR 50.46 and Appendix K, Research information letter 0202, 20 June 2002, ADAMS accession number ML021720744